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INTERPLAY BETWEEN SUPERCONDUCTIVITY AND ITINERANT FERROMAGNETISM IN Y_9Co_7 AT HIGH PRESSURE

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The theory of the interplay between superconductivity and itinerant ferromagnetism based on the single conduction band model in the mean field approximation is summarized. This theory predicts that superconductivity and itinerant ferromagnetism cannot co-exist, that the higher temperature magnetic phase can transform into the low temperature superconducting state, and that a superconducting state will not transform into a ferromagnetic state at a temperature below the superconducting transition. For the magnetic superconductor Y_9Co_7 we have reviewed the experimental results and in particular, we have shown that pressure suppresses magnetism resulting in a higher superconducing transition temperature and have concluded that Y_9Co_7 is an itinerant magnet. Pressure also sharpens the superconducting transition and increases the upper critical field, signifying that the ferromagnetic correlations and superconducting fluctuations co-exist but very spatially. For pressures greater than 5 kbar, the magnetoresistance is always positive, further indicating the suppression of magnetism by high pressure. Several microscopic experiments and some improvement in theory are suggested.

INTRODUCTION

For the past several years the interplay between superconductivity and magnetism has attracted considerable interest.[1-3] To date most of the studies, experimental as well as theoretical, have concentrated on the rare earth ternaries whose particular crystal structure gives rise to weak magnetic interactions between the localized magnetic moments arising from 4f rare earth ions and the superconducting d-electrons of the transition metal, i.e. separate electrons are responsible for superconductivity and magnetism, respectively.[3] Recently a new intermetallic magnetic superconductor, Y_9Co_7, has been intensively investigated.[4-14] In this compound, in contrast to the well-established ternary superconductors, magnetism is itinerant in nature and superconductivity appears at $T \sim 3K$) which is below the temperature at which the compound becomes magnetic ($T_m \sim 6K$). The measurements on this compound have yielded interesting results replete with anomalies. The detailed experimental investigations have concluded that ferromagnetic correlations which develop at higher temperatures remain finite and that magnetism is confined by superconductivity. Neutron depolarization studies have led to the conclusion of the presence of a "hybrid" state with the inhomogeneous spatial variation of the order parameter.

In our previous studies, we have shown that unusual Fermi surfaces are very sensitive to external pressure, [15] and that itinerant magnetism could be easily suppressed by high pressure.[16] Furthermore, owing to the fact that the application of high pressure is a useful approach to study the interplay between superconductivity and magnetism,[17] the electrical resistance and the magnetic susceptibility in Y_9Co_7 have been measured up to $\sim$20 kbar.[14] The experimental results have led to the conclusion that high pressure suppresses the magnetic correlation raising the superconducting transition temperature T_s.

In this paper, we briefly describe the theoretical aspect of the problem based upon a single-band conduction election model in a mean field approximation. We also discuss some salient features of the current experimental results. Finally, the experimental results at high pressure (up to 20 kbar) and at high magnetic field (up to $\sim$6T) will be presented.

SUMMARY OF THEORETICAL RESULTS

The theoretical aspects of the interplay between itinerant ferromagnetism and superconductivity were first investigated by Nakanishi, et al [18] employing the mean field approximation. They studied the interchange of the itinerant ferromagnetic and superconducting phases. Very recently, Lei, et al[19] have calculated the free energies at the same level of approximation by using a single-band model in which ferromagnetism and superconductivity arise from the same electrons. The superconducting part was treated by the BCS theory and the ferromagnetic part made use of the Hartree-Fock approximation. These authors have shown that the co-existent state in which itinerant ferromagnetism and superconductivty co-exist uniformly in space has the highest free energy and is thus unstable. Therefore in this model, the co-existent state cannot appear as a thermodynamically stable state. They have also found that the stability of the ferromagnetic state against the superconducting state depends on the parameters involved. When the parameters are chosen so that the ferromagnetic transition temperature in the absence of superconductivity, T_{mo}, is much higher than the superconducting transition temperature in the absence of magnetism, T_{so}, the free energy of the ferromagnetic state is lower than that of the superconducting state for $T<T_s$ and the state of the system is ferromagnetic; superconductivity does not appear. For T_{mo} higher, but not much higher, than T_{so}, their results show that there is a ferromagnetic to superconducting transition at $T_s<T_{so}$ and the transition is first order. Figure 1 displays the temperature dependence of the ferromagnetic order (magnetization), M, and the superconducting order, Δ, under this situation. The same result has been obtained in Ref. 18. For $T_{mo}<T_{so}$ and $T<T_{so}$, the superconducting state is more stable than the ferromagnetic state, and therefore ferromagnetism cannot re-enter once the superconductivity is already present. These results are quite contrary to the re-entrant ferromagnetic ternaries [3] where superconductivity occurs at higher temperature followed by the appearance of ferromagnetism at lower temperature. In these ternaries ferromagnetism arises from the localized 4f-electrons while superconductivity comes from the d-electrons and the free energies of these two ordered states can be regarded independent of each other and they can take whatever values the system allows them to have.

It should be noted that the single-band model may not be applicable to a real system. There has been speculation that in Y_9Co_7 the 4d-electrons of Y are responsible for superconductivity and the 3d-electrons of Co for magnetism. In this case a more sophisticated theory than the single-band model is needed. Moreover, the mean field approximation does not take into consideration superconducting fluctuations. Therefore, the co-existance of superconducting fluctuations with itinerant ferromagnetism above T_s, as suggested by some experimental results [10,11] does not contradict the present theory.

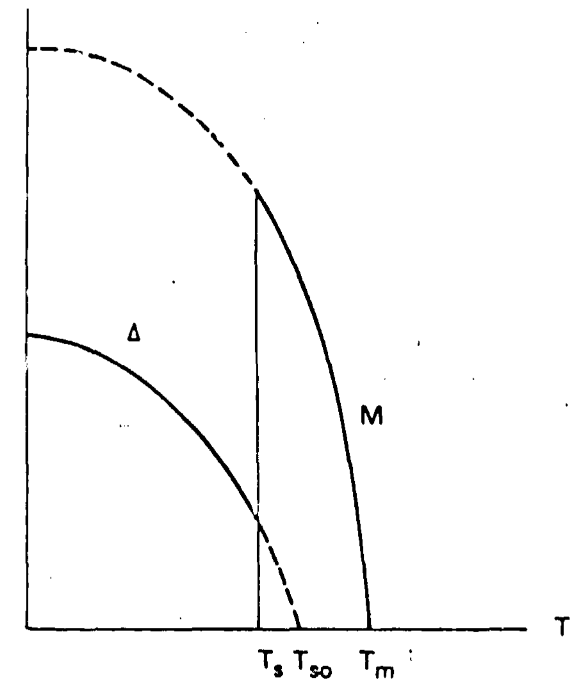

Fig. 1 Temperature dependencies of the superconducting order-parameter, Δ and the magnetization, M, when the magnetic transition temperature, T_m, is higher than the superconducting transition temperature, T_s. Here T_s is lower than T_{so} the transition temperature when magnetism is absent.

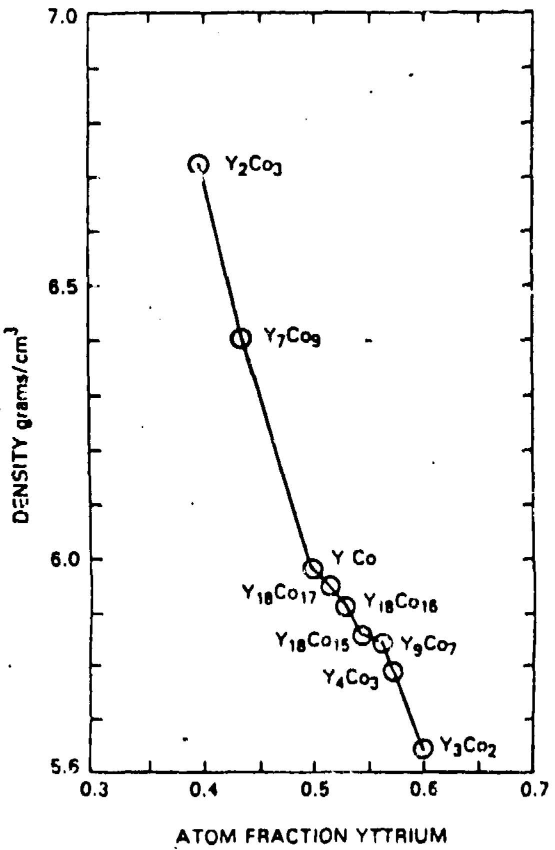

Fig. 2 Diagram of density of alloys vs yttrium atom fraction.

SAMPLES

Y_9Co_7 crystallizes with an hexagonal unit cell [20] resulting from the assembly of Y atoms in the form of trigonal prisms. A group of four Co atoms is enclosed within the center of each of the Y prisms. The remainder of the Co atoms lie along the c-axis of the unit cell. From the detailed study of this compound [10,11] some properties seem to be sensitive to the inhomogeneity and purity of the sample. The occurrence of superconductivity and magnetism depends strongly on the Y_9Co_7 crystal structure. The phase diagram of the Y-Co binaries has been investigated by Grover, et al [21]. Their results show the existence of a single phase over a narrow composition range of Y_9Co_7. For the Y_4Co_3 composition which was originally studied and led to the discovery of Y_9Co_7, the hexagonal Y_9Co_7 phase persists with Y_8Co_5 as an impurity phase in which Y_8Co_5 is not superconducting and shows no magnetic ordering.

When our work was initiated, the only published Y-Co phase diagram was that of Ray.[22] Early work on the magnetic and superconducting properties in this system indicated that there was a question as to the compound composition of the superconducting phase. Because compound occurrences can be determined as a function of composition by the breaks in density vs composition diagrams, a series of alloys was prepared and heat treated for 336 hours at 530°C. The alloy densities were determined by weighing the buttons in bromobenzene. The results of these determinations are plotted in Fig. 2. With the possible exception of the point at $Y_{18}Co_{15}$, the changes in slope of density vs yttrium atom fraction at Y_2Co_3, YCo, and Y_9Co_7 are consistent with the new phase diagram published by Grover et al.[21] As a result,

Y_9Co_7 appears tc exirt as a single phase.

PRL 'JS EXPERIMENTAL RESULTS

. jure 3 shows the results of the ac magnetic susceptibility, χ, and electr. al resistance, R, obtained by Sarkissian.[11] In this sample superconductivity sets in at ∿3K and the magnetic transition takes place at ∿6K. It is ev dent that thermal .ysteresis is present in the magnetic region. This author has also shown the current dependence of the electrical resistance in the magnetic region, [10] strongly indicating that superconducting interactions co-exist with strong magnetic correlation. In addition, he has measured the magnetoresistance in the magnetic and superconducting state. At low temperature but above the superconducting transition, the low field magnetoresistance indicates that superconducting fluctuations are present. This observation further suggests that the superconducting interactions are present in the magnetic region.

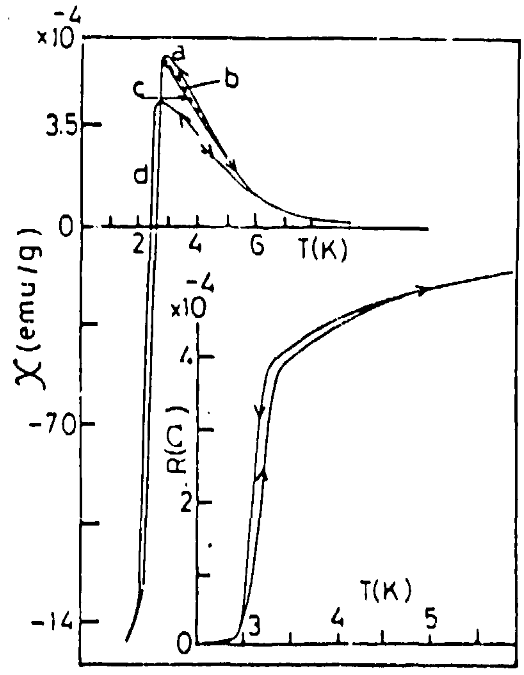

Fig. 3 Temperature dependence of the ac susceptibility, χ, in Y_9Co_7. The arrows indicate in which direction the temperature was varied. a) cooling down from 4.2K to 1.5K, b) and c) second and third warming cycles and d) χ in the same sample before further low temperature annealing. The inset shows the resistance data. (From Ref. 11).

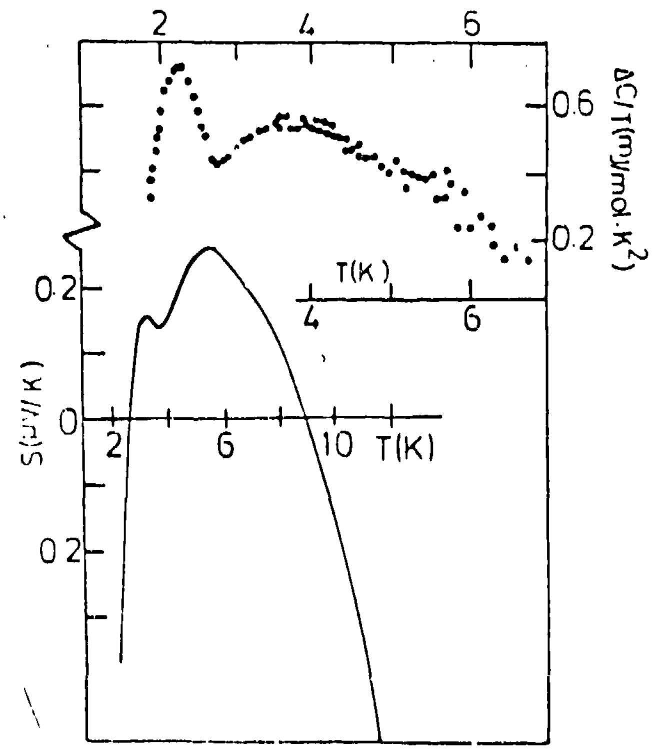

Fig. 4 Excess heat capacity ΔC/T and thermopower S of Y_9Co_7. (From Ref. 11).

In addition to the transport properties, Sarkissian has measured the magnetization in magnetic fields from H∿ 1 Gauss to 200 Gauss.[10,23] According to his data, there is no sign of linear behavior in M^2 and M/H plots in the low field regime. The magnetic susceptibility at high temperatures does not follow a Curie-Weiss law but rather tends to temperature-independence, as expected for an itinerant magnet. This result is consistent with the observation that the temperature dependence of the high temperature resistance is less than a linear rise with temperature. Moreover, his M-H hysteresis loops, taken in fields up to 200 Gauss, have enabled him to observe the Meissner effect. From his observation that the hysteresis loop is more pronounced below T_s, he has concluded that the hysteresis is, at least partly, due to superconductivity not just ferromagnetic domain walls as in an ordinary magnet.

The heat capacity and thermopower are the best demonstration of bulk superconductivity. Figure 4 from Ref. 11 shows the excess heat capacity $\Delta C/T$, after substracting lattice and electronic contribution. The peak at $\sim$2.5K clearly displays the bulk superconducting transition. The peak in the thermopower, S, around 3K is also consistent with this transition.

Among the salient features in Y_9Co_7, the results of the depolarization of polarized neutrons [10,11] are particularly interesting. Sarkissian has shown that the depolarization is present only when the magnetic field is applied perpendicular to the incident neutron polarization. The abrupt onset of depolarization takes place below 4K, displaying the kind of behavior to be expected if inhomogeneities were forming in the temperature region in which magnetic correlations are present. This inhomogeneity is consistent with the "hybrid" state present in the magnetic region discussed above. The finite depolarization below T_s has been observed, but, because of the possible depolarization originating from the flux line domains, the question of complete or partial suppression of magnetic correlations could not be answered.

EXPERIMENTAL RESULTS

The Y_9Co_7 samples used in our high pressure experiments were prepared by Johnson, Matthy and Co. 99.999% pure cobalt and 99.99% yttrium from the Research Chemical Co. The alloys were made by arc melting together weighed amounts of cobalt and yttrium metals on a water-cooled copper hearth in a gettered argon atmosphere. The buttons were turned and remelted ten times to insure compositional homogeneity. Melting losses did not exceed 0.4% so that the compositions were taken to be those as weighed out. The samples were heat treated for 20 days at 530±5°C in a high vacuum furnace. Chemical analysis, within limits of the atomic adsorption method used, shows the material to have tne composition Y_9Co_7. Powder x-ray diffraction patterns were taken on the samples. All the observed lines could be indexed on the structure, "Y_4Co_3" reported by Lamaire, et al.[20] Within the sensitivity ($\sim$5%) the alloys at Y_9Co_7 were single phase. The resistivity ratio ($R_{300}/R_{4.2}$) of our samples is $\sim$16, comparable with others.[10,11] The T_c of our samples is about 0.5K lower than those used in Refs. 10 and 11 possibly because of the presence of Gd impurities ($\sim$100 ppm) in yttrium. However, this lower T_c should not seriously effect our high pressure studies.

We have simultaneously measured the electrical resistance and ac magnetic susceptibility of the samples as a function of temperature from $\sim$1.2K to 300K, at pressures up to $\sim$20 kbar and magnetic fields up to 6T. The resistance was measured using a standard four-terminal ac technique at 33 Hz, while a 610 Hz susceptibility signal was obtained from a secondary coil wrapped directly around the sample. The pressure was generated in a 1:1 fluid mixture of n-pentane and isoamyl alchol contained inside a 3.2 mm diameter Teflon cup enclosed inside a beryllium-copper cell, employing the self-clamped technique. The pressure was monitored by a lead manometer with an accuracy of ± 1 kbar. A superconducting magnet capable of generating a magnetic field up to 6T was employed for the magnetic field studies.

The temperature dependence of the ac magnetic susceptibility at various values of pressure is displayed in Fig. 5.[24] The increase of the susis more pronounced below T_s, he has concluded that the hysteresis is, at least partly, due to superconductivity not just ferromagnetic domain walls as in an ordinary magnet.

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The temperature dependence of the ac magnetic susceptibility at various values of pressure is displayed in Fig. 5.[24] The increase of the susceptibility below $\sim$8K at ambient pressure, in accordance with previous reports, [10,11] indicates the onset of ferromagnetic correlations. Similar to other itinerant ferromagnets, [16] χ decreases with increasing pressure. Also shown in the figure is the increase of the superconducting transition temperature with increasing pressure, consistent with the observation that magnetism, which depresses T_s, is suppressed by the applied pressure.

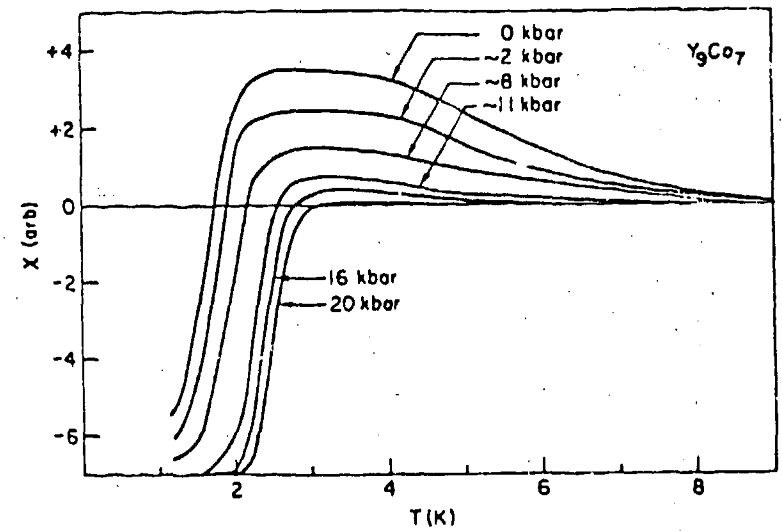

Fig. 5 Magnetic susceptibility, χ, vs T at various pressure values.

Figure 6 shows the temperature dependence of electrical resistance at various pressures. It is particularly intriguing to observe that the resistance is independent of pressure up to $\sim$20 kbar for T>8K. This pressure independence seems to indicate that the magnetic correlations exist only for T<8K. As can be seen, the higher the pressure, the sharper the transition, very similar to the pressure dependence of X near the transition shown in Fig. 5. This interesting experimental result indicates that, the ferromagnetic correlations and superconducting fluctuations at ambient pressure, co-exist around T_s but vary spatially (the "hybrid" state), in agreement with suggestions in Refs. 10 and 11. Furthermore at high pressure, the magnetism is suppressed and the sample becomes more "uniform" spatially, giving rise to a sharper transition.

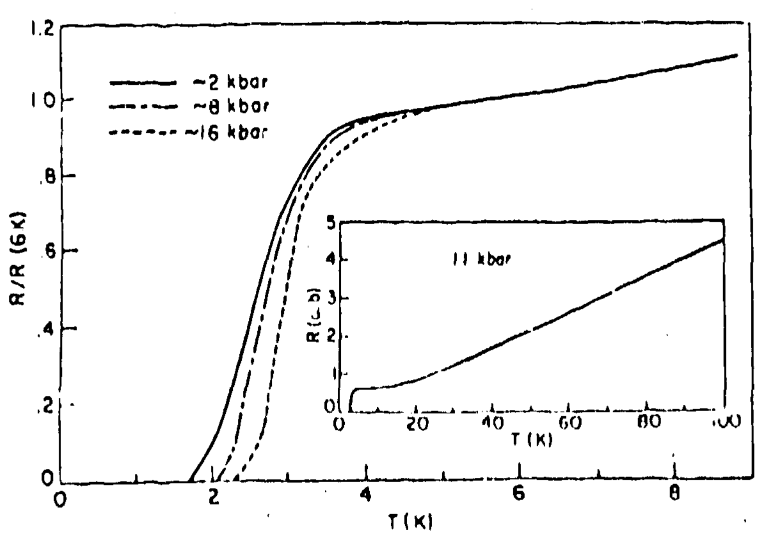

Fig. 6 Resistance, R, (with respect to R at 6K) vs T at $\sim$3 kbar, $\sim$8 kbar, and $\sim$16 kbar. Inset shows R vs T at $\sim$11 kbar.

We have also measured the resistance as a function of an external magnetic field up to 6 T. Figure 7 exhibits some of our data at $\sim$15 kbar and Fig. 8 demonstrates the field dependence of R at 1.25K and 2.5K at various values of pressure. It is striking to note that the magnetoresistance for pressures > 6 kbar is always positive for T<4.2K, in constrast to the ambient pressure result that the magnetoresistance is negative.[10] However, this field dependence is in accordance with an earlier conclusion that pressure suppresses magnetism thus reducing the (negative) magnetoresistance. In want of an appropriate theory for the critical field of a magnetic superconductor, we define the midpoint of the transition as the upper critical field, H_{c2} (following Ref. 17). Figure 9 shows H_{c2} vs T at various values of pressure. As expected, H_{c2} increases with increasing pressure.

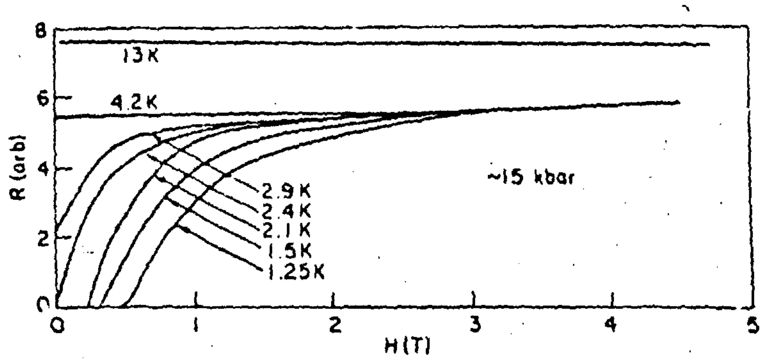

Fig. 7 Resistance, R, vs the magnetic field, H, at various temperatures at 15 kbar.

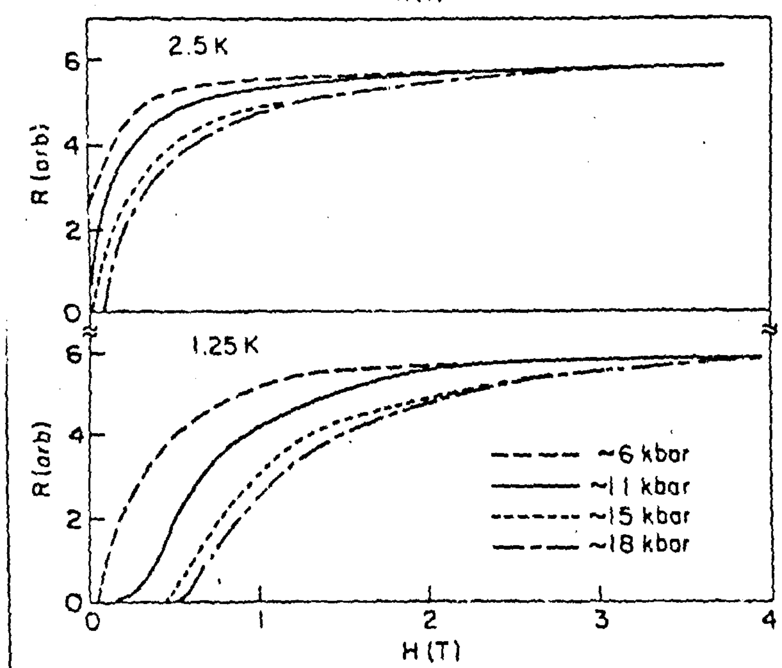

Fig. 8 Resistance, R, vs H at various values of pressure and temperature.

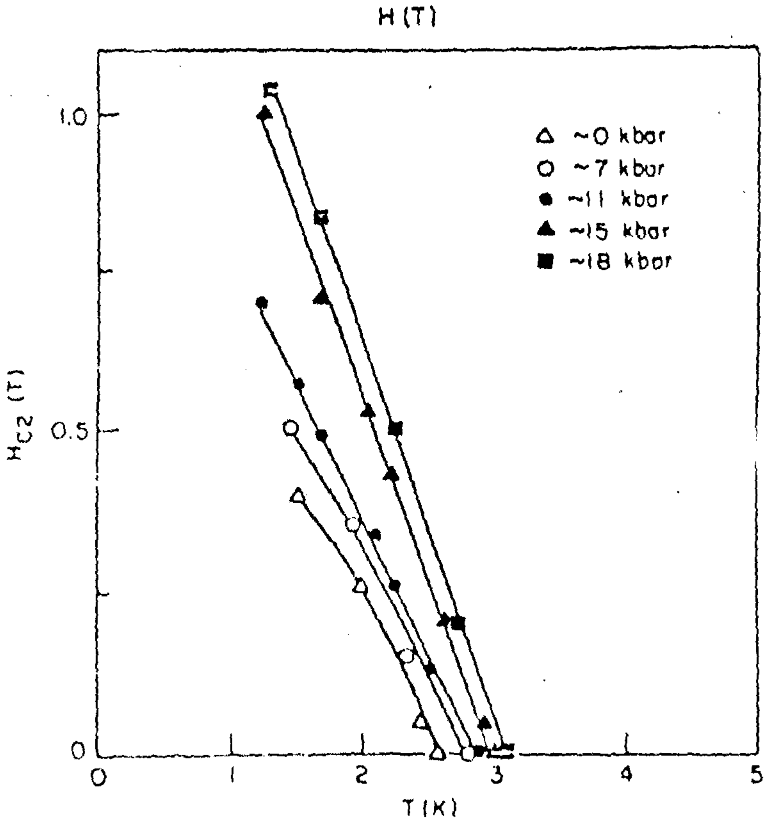

Fig. 9 Critical field, H_{c2}, vs T at various values of pressure.

DISCUSSIONS AND CONCLUSIONS

Our high pressure experiment has yielded the following results: a) high pressure strongly suppresses magnetism; b) the magnetism is itinerant; c) T_s and H_{c2} increase with pressure; d) the superconducting transition is sharper at higher pressures; e) the magnetoresistance for pressure greater than 8 kbar and temperatures lower than 5K is always positive; and f) the ferromagnetic correlations and superconducting fluctuations co-exist around T_s in the magnetic region and they vary in space. It is interesting to note that some of these results can be interpreted in terms of Fig. 1 in which the superconducting transition, T_{so}, is depressed because of the presence of magnetism. Upon the application of high pressure, magnetic interactions are suppressed, thus raising T_s toward T_{so}. This result suggests the need to repeat our experiments at much higher pressure.

The question of the possible co-existence of superconductivity and magnetic correlations, as hinted by the neutron scattering results discussed above, has to be answered. A better neutron scattering experiment is obviously necessary; this requires the preparation of single crystal Y_9Co_7. Furthermore, microscopic studies such as NMR, muon spin resonance and relaxation, ultrasonic attenuation, tunneling, microwave impedence, and the Mössbauer effect are needed to understand the intriguing physical properties in Y_9Co_7.

Beyond doubt, the band calculations are essential. In order to understand Y_9Co_7, a detailed theory taking into account the magnetic correlations of the 3d-electrons of Co and the superconducting pairing in the 4d-electrons of Y should be vital. It is also important for the theory to go beyond the mean field approximation to include superconducting fluctuations and electromagnetic effects [3] and to calculate the physical quantities obtainable from the experiments suggested above.

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23. Similar results have been obtained in Ref. 13.
24. In Ref. 13, χ was measured up to 4.7 kbar.